

CLAIMS

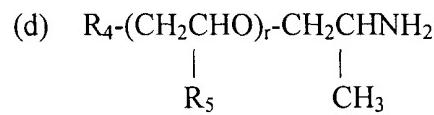
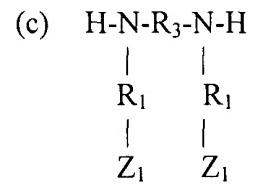
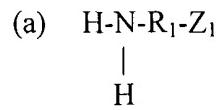
1. A method of modifying the permeability to water of a subterranean formation comprising injecting into the subterranean formation an aqueous composition comprising from about 0.005 percent to about 2 percent, by weight, of a water-soluble alkylene oxide branched polyhydroxyetheramine or a salt thereof, wherein the alkylene oxide branched polyhydroxyetheramine is prepared by reacting a diepoxide with one or more alkylene oxide functionalized amines and one or more amines having two reactive hydrogen atoms and optionally reacting the resulting polyhydroxyetheramine with an acid or alkylating agent to form the salt.

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2. The method of claim 1 wherein the diepoxide is selected from the group consisting of diglycidyl esters of diacids, diglycidyl ethers of diols, diglycidyl ethers of polyols and epoxidized olefins.

15 3. The method of claim 1 wherein the diepoxide is selected from the group consisting of diglycidyl ethers of polyhydric phenols.

4. The method of claim 1 wherein the alkylene oxide functionalized amine is selected from the group consisting of amines of formula (a)-(d)



5 wherein

R_1 is independently selected at each occurrence from a group of formula $(-\text{CH}_2-\text{CH}_2-\text{O}-)_p$ and a group of formula $(-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-)_q$ or a mixture thereof;

10 R_3 is $\text{C}_2\text{-C}_{20}$ alkylene optionally substituted with alkylamido, hydroxy, alkoxy, halo, cyano, aryloxy, alkylcarbonyl or arylcarbonyl;

R_4 is alkoxy;

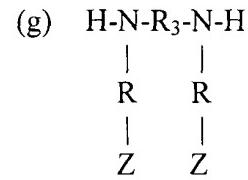
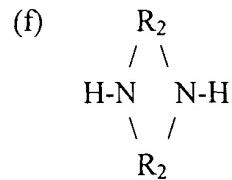
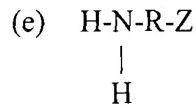
R_5 is H or $-\text{CH}_3$;

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Z_1 is independently selected at each occurrence from hydrogen, $\text{C}_1\text{-C}_7$ alkyl and acyl; and

n, p, q and r are independently integers of 1 to about 45.

5. The method of claim 1 wherein the amine having two reactive hydrogen atoms is selected from the group consisting of amines of formula (e)-(g)



5 wherein

R is C₂-C₃₀ alkylene, optionally substituted with one or more hydroxy or hydroxyalkyl groups;

R₂ is C₂-C₁₀ alkylene, optionally substituted with alkylamido, hydroxy, alkoxy, cyano, dialkylamine, aryloxy, alkylcarbonyl or arylcarbonyl;

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R₃ is C₂-C₂₀ alkylene optionally substituted with alkylamido, hydroxy, alkoxy, halo, cyano, aryloxy, alkylcarbonyl or arylcarbonyl; and

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Z is hydrogen, alkylamido, hydroxy, dialkylamine, alkoxy, aryloxy, cyano, alkylcarbonyl, or arylcarbonyl;

6. The method of claim 5 wherein R is methylene or ethylene; R₂ is ethylene; R₃ is C₂-C₂₀ alkylene optionally substituted with alkylamido, dialkylamino, hydroxy or alkoxy; and Z is alkylamido, dialkylamino, hydroxy or alkoxy.

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7. The method of claim 5 wherein the amine having 2 reactive hydrogen atoms is selected from the group consisting of methylamine; ethylamine; propylamine; butylamine; sec-butylamine; isobutylamine; 3,3-dimethylbutylamine; hexylamine; benzylamine; 2-amino-1-butanol; 4-amino-1-butanol; 2-amino-2-methyl-1-propanol; 6-amino-1-hexanol; ethanolamine; 5 propanolamine; tris(hydroxymethyl)aminomethane; 1-amino-1-deoxy-D-sorbitol; 3-amino-1,2-propanediol; 2-amino-2-methyl-1,3-propanediol; 2-amino-2-ethyl-1,3-propanediol; 3-(dimethylamino)propylamine; *N,N*-dimethylethylenediamine; *N,N*-diethylethylenediamine; 1-(2-aminoethyl)piperidine; 4-(2-aminoethyl)morpholine; 2-(2-aminoethyl)-1-methylpyrrolidine; 1-(2-aminoethyl)pyrrolidine; 2-(2-aminoethyl)pyridine; 2-(2-aminoethoxy)ethanol; 10 2-(2-aminoethylamino)ethanol; piperazine, 2-methylpiperazine, 2,6-dimethylpiperazine; 2-(methylamido)piperazine; *N,N'*-bis(2-hydroxyethyl)ethylenediamine, *N,N'*-dimethylethylenediamine, *N,N'*-dimethyl-1,4-phenylenediamine and *N,N'*-dimethyl-1,6-hexanediamine.
- 15 8. The method of claim 2 wherein the diglycidyl esters of diacids, diglycidyl ethers of diols, diglycidyl ethers of polyols and epoxidized olefins are selected from the group consisting of diglycidyl ether of dimer acid, bis(2,3-epoxypropyl)ether, diglycidyl ether of 1,4-butanediol, diglycidyl ether of neopentyl glycol, diglycidyl ether of ethylene glycol, glycerol diglycidyl ether, diglycidyl ether of sorbitol, diglycidyl ether of trimethylol propane, diglycidyl ether of 20 polyethyleneglycols, diglycidyl ether of polypropylene glycols, diglycidyl ether of glycols from the reaction of ethylene oxide with propylene oxide, diglycidyl ether of cyclohexane dimethanol, 1,2,3,4-diepoxybutane; 1,2,7,8-diepoxyoctane, 1,2,9,10-diepoxydecane, 1,2,5,6-diepoxyoctane and the like.

9. The method of claim 3 wherein the diglycidyl ether of a polyhydric phenol is selected from diglycidyl ethers of resorcinol; catechol; hydroquinone; bisphenol A; bisphenol F; bisphenol E; bisphenol K; 4,4'-dihydroxydiphenyl sulfide; bisphenol S; 4,4'-thiodiphenol; 2,6-dihydroxynaphthalene; 1,4'-dihydroxynaphthalene; 9,9-bis(4-hydroxyphenyl)fluorene;
- 5 dihydroxy dinitrofluorenylidene; diphenylene; 2,2-bis(4-hydroxyphenyl)-acetamide; 2,2-bis(4-hydroxyphenyl)ethanol; 2,2-bis(4-hydroxyphenyl)-*N*-methylacetamide; 2,2-bis(4-hydroxyphenyl)-*N,N*-dimethylacetamide; 3,5-dihydroxyphenyl-acetamide; 2,4-dihydroxyphenyl-*N*-(hydroxyethyl)-acetamide; 2,2-bistris-hydroxyphenyl methane; 2,6,2',6'-tetrabromo-p,p'-bisphenol A; 2,6,2',6'-tetramethyl-3,5,3'-tribromo-p,p'-biphenol;
- 10 2,6,2',6'-tetramethyl-3,5,3'5'-tetrabromo-p,p'-biphenol; tetramethylbiphenol; 4,4'-dihydroxydiphenylethylmethane; 3,3'-dihydroxydiphenyldiethylmethane; 3,4'-dihydroxydiphenylmethylpropylmethane; 4,4'-dihydroxydiphenyloxide; and 4,4'-dihydroxydiphenylcyanomethane.
- 15 10. The method of claim 3 wherein the diglycidyl ether of a polyhydric phenol is selected from the diglycidyl ethers of bisphenol A, 4,4'-sulfonyldiphenol, 4,4'-oxydiphenol, 4,4'-dihydroxybenzophenone, 9,9-bis(4-hydroxyphenyl)fluorene and bisphenol F.
- 20 11. The method of claim 3 wherein the diglycidyl ether of a polyhydric phenol is the diglycidyl ether of bisphenol A.
12. The method of claim 2 wherein the diglycidyl ether of a diol is diglycidyl ether of neopentyl glycol.
- 25 13. The method of claim 2 wherein the diglycidyl ethers of polyols are selected from diglycidyl ethers of glycerol.
14. The method of claim 2 wherein the epoxidized olefin is 1,2,3,4-diepoxybutane.

15. The method of claim 2 wherein the diglycidyl ester of a diacid is diglycidyl ether of dimer acid.
16. The method of claim 1 wherein the water-soluble alkylene oxide branched polyhydroxyetheramine comprises secondary amine, tertiary amine or ditertiary amine end groups.
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17. The method of claim 16 wherein the water-soluble alkylene oxide branched polyhydroxyetheramine comprising secondary amine, tertiary amine or ditertiary amine end groups is prepared by reacting a diepoxide with one or more alkylene oxide functionalized amines and one or more amines having two reactive hydrogen atoms to form the water-soluble alkylene oxide branched polyhydroxyetheramine and then reacting the water-soluble alkylene oxide branched polyhydroxyetheramine with one or more amines having one or two reactive hydrogen atoms.
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18. The method of claim 16 wherein the water-soluble alkylene oxide branched polyhydroxyetheramine comprising secondary amine, tertiary amine or ditertiary amine end groups is prepared by reacting a diepoxide with one or more alkylene oxide functionalized amines and one or more amines having two reactive hydrogen atoms and an amine having 3 or more reactive hydrogen atoms to form the water-soluble alkylene oxide branched polyhydroxyetheramine and then reacting the water-soluble alkylene oxide branched polyhydroxyetheramine with one or more amines having one or two reactive hydrogen atoms.
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19. The method of claim 1 wherein the water-soluble alkylene oxide branched polyhydroxyetheramine is prepared by reacting a mixture of diepoxide and one or more aliphatic or aromatic triepoxides with one or more alkylene oxide functionalized amines, one or more amines having two reactive hydrogen atoms to impart cross linking.
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20. The method of claim 1 wherein the water-soluble alkylene oxide branched polyhydroxyetheramine salt is prepared by reacting a mixture of diepoxyde and one or more aliphatic or aromatic triepoxides, one or more alkylene oxide functionalized amines, one or more amines having two reactive hydrogen atoms to impart cross linking and then an acid or alkylating agent.

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21. The method of claim 1 wherein the aqueous composition further comprises about 1 to about 10 weight percent of one or more clay stabilization salts.

22. The method of claim 21 wherein the clay stabilization salts are selected from KCl, NaCl, NaBr,
10 sodium acetate and NH₄Cl.

23. An aqueous composition comprising from about 0.005 percent to about 2 percent, by weight, of a water-soluble alkylene oxide branched polyhydroxyetheramine or a salt thereof and about 0.005 to about 2 percent by weight of one or more solubilizing agents, wherein the alkylene oxide branched polyhydroxyetheramine is prepared by reacting a diepoxyde and optionally one or more aliphatic or aromatic triepoxides with one or more alkylene oxide functionalized amines and one or more amines having two reactive hydrogen atoms and optionally reacting the resulting polyhydroxyethermaine with an acid or alkylating agent to form the salt.

20 24. The aqueous composition of claim 23 wherein the solubilizing agent is selected from isopropanol, butanol, 1,2-propylene glycol, ethylene glycol, hexylene glycol, N,N-dimethylformamide, N,N-dimethylacetamide, ethylene glycol butyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, di(propylene glycol) methyl ether, propylene glycol phenyl ether and propylene glycol methyl ether.

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25. The aqueous composition of claim 23 further comprising about 1 to about 2 weight percent of one or more clay stabilization salts.

26. An aqueous composition comprising about 10 percent to about 50 weight percent of one or more water-soluble, alkylene oxide branched polyhydroxyetheramines or a salt therof and about 1 to about 90 weight percent of one or more solubilizing agents, wherein the alkylene oxide branched polyhydroxyetheramine is prepared by reacting a diepoxide and optionally one or more aliphatic or aromatic triepoxides with one or more alkylene oxide functionalized amines and one or more amines having two reactive hydrogen atoms and optionally reacting the resulting polyhydroxyetheramine with an acid or alkylating agent to form the salt.
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27. The aqueous composition of claim 26 comprising about 10 to about 30 weight percent of one or more solubilizing agents.
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28. The aqueous composition of claim 26 wherein the solubilizing agent is selected from isopropanol, butanol, 1,2-propylene glycol, ethylene glycol and hexylene glycol, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, ethylene glycol butyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, di(propylene glycol) methyl ether, propylene glycol phenyl ether and propylene glycol methyl ether.
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29. A water-soluble alkylene oxide branched polyhydroxyetheramine salt prepared by reacting a diepoxide with one or more alkylene oxide functionalized amine and one or more amines having 2 reactive hydrogen atoms and then reacting the resulting polyhydroxyetheramine with an acid or alkylating agent.
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30. The water-soluble alkylene oxide branched polyhydroxyetheramine salt of claim 29 wherein the alkylating agent is methyl chloride or dimethyl sulfate.

31. A water-soluble alkylene oxide branched polyhydroxyetheramine salt comprising secondary amine, tertiary amine or ditertiary amine end groups prepared by reacting a diepoxide with one or more alkylene oxide functionalized amine and one or more amines having 2 reactive hydrogen atoms and then reacting the resulting polyhydroxyetheramine with one or more amines having one or two reactive hydrogen atoms followed by an acid or alkylating agent.
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32. A water-soluble alkylene oxide branched polyhydroxyetheramine salt comprising secondary amine, tertiary amine or ditertiary amine end groups prepared by reacting a diepoxide with one or more alkylene oxide functionalized amine, one or more amines having 2 reactive hydrogen atoms and an amine having 3 or more reactive hydrogen atoms and then reacting the resulting polyhydroxyetheramine with one or more amines having one or two reactive hydrogen atoms followed by an acid or alkylating agent.
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